

[JP,11-158681,A]

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CLAIMS

[Claim(s)]

[Claim 1]To this cathode room of a fluid bed type cell which accommodated a conductive particle which supported 1 or two or more platinum metals in this cathode room of a cell divided by a septum in a positive pole room and a cathode room. A disposal method of selenium content processed water supplying and electrolyzing processed water containing 6 value selenium, returning said 6 value selenium, and considering it as metal selenium or an insoluble selenium compound.

[Claim 2]A way according to claim 1 a platinum metal is palladium.

[Claim 3]A way according to claim 1 pH of processed water is 0.5-3.0.

[Claim 4]A conductive fiber which supported 1 or two or more platinum metals is accommodated in this cathode room of a cell divided by a septum in a positive pole room and a cathode room, A disposal method of selenium content processed water energizing supplying processed water containing 6 value selenium to this cathode room, returning said 6 value selenium, and considering it as metal selenium or an insoluble selenium compound.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the method for carrying out reduction removal of the 6 value selenium with removal more difficult for details by reduction

processing in electrolysis from waste fluid about the method of carrying out reduction removal of the selenium in electrolysis from selenium content processed water.

[0002]

[Description of the Prior Art] Naturally, selenium (Se) is contained in small quantities in sulfur or a sulfide, and is produced. In waste fluid, such as refinement including copper, it contains with the gestalt of the ion of SeO_3^{2-} (tetravalent selenium), In addition, SeO_4^{2-} (6 value selenium) ion is also contained in said waste fluid, and the former tetravalent selenium is in the tendency for it to be changed into 6 value selenium in waste fluid, and for 6 value selenium concentration in waste fluid to become high. Selenium is a toxic substance and it is not allowed to discharge from a viewpoint of environmental protection, if it removed out of said waste fluid and also is not in the eye of the law. It is reported among said tetravalent selenium and 6 value selenium that removal of tetravalent selenium can be performed comparatively easily, For example, add Fe^{2+} by pH 3-5 to said tetravalent selenium compound ion (SeO_3^{2-}), and this Fe^{2+} is oxidized by this tetravalent selenium ion, By hydrolyzing, promote reduction of tetravalent selenium, metallic iron or an iron compound, metal selenium, or a selenium compound is made to coprecipitate, and removal of the tetravalent selenium out of waste fluid is performed (JP,48-30558,B). However, this method cannot be applied to weak 6 value selenium of reduction nature, but the method of returning to metal selenium or an insoluble selenium compound, and collecting these 6 value selenium from the former using stronger drugs, is tried by removal of 6 value selenium.

[0003] For example, in JP,5-78105,A, to the ability of tetravalent selenium to remove with a described method 6 value selenium, If a powerful reducing agent is not used in a strong acid solution, not being deposited as metal selenium is indicated, the compound which reacts to this gazette with said tetravalence and 6 value selenium ion further, and generates a poorly soluble salt is added in waste fluid, and the method of removing said selenium ion in two steps is proposed. When a copper ion lives together in waste fluid, this method cannot be used, but a neutralizer, acid, and iron ion are added (JP,6-79286,A). However, in order to remove from the waste fluid whose drugs which were inferior to economical efficiency and were added since these methods needed two processes and addition drugs were needed like former art have been processed thoroughly, there is a problem that the further operation is needed.

[0004] The removing method of selenium ion which returns the waste fluid containing selenium ion in electrolysis is also indicated (U.S. Pat. No. 5,322,600 specification). This method to the cell which accommodated sheet shaped anode and negative pole fundamentally. In order to mean supplying the waste fluid containing selenium ion and

removing selenium ion as insoluble metal or a compound and to increase an electrode area, it is indicated that an electrode chamber may be filled up with graphite particles or allied substances. However, there is no statement about making graphite etc. support metal, such as palladium, in this U.S. Kuniaki thin document. The special diffusion shell (semipermeable membranes) is used as barrier membrane, liquid is circulated in order of a cathode room -> diffusion-shell -> positive pole room, and the selenium ion of -2 value is oxidized in a positive pole room, and he returns the selenium ion of tetravalence and 6 values, and is trying to collect in a cathode room. Thus, in order to perform reduction or oxidation of selenium ion at a two-poles room, an electrolysis solution will penetrate barrier membrane and it will pass through a two-poles room, The expensive diffusion shell is needed, if operation is continued, blinding of this diffusion shell is also produced, a maintenance is needed, and also in order to make the diffusion shell penetrate an electrolysis solution, the above pressure is required, and there is a fault that a large-sized pump must be installed. Although it is indicating that this invention may fill up an electrode chamber with graphite etc., It is not shown clearly how many 6 value selenium the initial concentration and the electrolytic condition of 6 value selenium are unknown only by a sheet shaped electrode being used fundamentally and moreover an example having the statement "tetravalent selenium and 6 value selenium are returned to metal selenium in electrolysis", and are actually returned. When this invention person tried reduction of 6 value selenium with the fixed-bed cell filled up with activated carbon as mentioned later, this reduction hardly took place but it turned out that it is not practical.

[0005]

[Objects of the Invention]This invention does not need addition of drugs but an object of this invention is to provide the method and device for removing 6 value selenium from processed water, such as waste fluid, effectively moreover almost quantitatively.

[0006]

[Means for Solving the Problem]This invention which solves the above-mentioned problem to this cathode room of a fluid bed type cell which accommodated a conductive particle which supported 1 or two or more platinum metals in this cathode room of a cell divided by a septum in a positive pole room and a cathode room. A disposal method of selenium content processed water supplying and electrolyzing processed water containing 6 value selenium, returning said 6 value selenium, and considering it as metal selenium or an insoluble selenium compound, And a conductive fiber which supported 1 or two or more platinum metals is accommodated in this cathode room of a cell divided by a septum in a positive pole room and a cathode room, It is a disposal

method of selenium content processed water energizing supplying processed water containing 6 value selenium to this cathode room, returning said 6 value selenium, and considering it as metal selenium or an insoluble selenium compound.

[0007]This invention is explained in detail below. Processing of processed water, such as refinement waste fluid which uses this invention method or a device, uses a negative pole carrier which is negative pole carriers, such as a conductive particle which supported platinum metals, such as platinum, palladium, a ruthenium, iridium, and osmium, or textiles, especially a carbonaceous particle, or carbon fiber as the negative pole. In this invention, support of this platinum metal is indispensable and high removal efficiency is acquired by support of a platinum metal of the specified quantity, etc. to only removal efficiency of about a maximum of 20 to 30% being acquired in a mere negative pole carrier without support of this metal. In order that this invention may mean selenium removal in wide pH range, support of the above-mentioned platinum metal becomes indispensable, but even if it does not support a platinum metal with a highly acidic field of the pH 1.0 neighborhood, in it, reduction removal of 6 value selenium is possible. Since excess voltage of 6 value selenium which is hard to be returned in an electrolytic condition usual in 6 value selenium being returned by support of a platinum metal becomes smaller than the usual excess voltage by reduction ability which a platinum metal has, Except a highly acidic field, it can be surmised by a negative pole carrier without support of a platinum metal that 6 value selenium which is hard to be returned is what is returned to metal selenium through tetravalent selenium. Although especially this invention targets 6 value selenium, Since it oxidizes to tetravalence or divalent before an electrolysis start, it is returned to metal selenium by this invention and -2 value selenium can also be collected if tetravalent selenium and divalent selenium are also easily returned to metal selenium and acidity or alkalinity of processed water is made into acidity, selenium ion of all the valences can be collected substantially.

[0008]As for a conductive particle or textiles, as a negative pole carrier used for this invention, it is preferred to use a carbonaceous material, for example, activated carbon, graphite particles, the shape of felt, or commercial carbon fiber fabricated curdy. Although processed water is made to supply and flow from a lower part in this invention to a conductive particle with which it filled up in a cell as below-mentioned, even if a conductive fiber is accommodated in a cell and it supplies processed water from a lower part, for binding force between textiles, these textiles do not flow but are maintained with the fixed bed. Although platinum metals supported by this negative pole carrier may be supported with what kind of technique, it is desirable for an activated carbon

particle to be immersed in a solution which dissolved a chloride of a platinum metal, for example, and to make it stir and support it. An electrolysis solution may be electrolyzed as a platinum metal compound solution with a cell for selenium ion reduction mentioned later, and reduction support of said platinum metal may be carried out on the activated carbon particle surface. In addition, although a nonelectrolytic plating method and a thermal decomposition method are also employable depending on conditions, since it is easy to receive damage that said carrier is carbonaceous, it is preferred to adopt dip coating or an electrolytic decomposition process mentioned above. Although it depends for a holding amount of a platinum metal etc. on quantity etc. of selenium ion in waste fluid which should be processed, it is desirable to be referred to as 3-6g to 1 kg of negative pole carriers. Even if it makes quantity which reduction of 6 value selenium does not take place that it is less than 3g easily due to a short time, and exceeds 6 g support, efficiency will hardly improve, but economical efficiency will be missing. When electrolysis for selenium reduction is continued, a platinum metal of negative pole carrier surfaces, such as activated carbon, etc. may be exhausted, and catalytic activity may fall, but. In that case, an electrolysis solution of a cell which accommodated a negative pole carrier which was exchanged for the new negative pole carrier prepared independently, or was exhausted is electrolyzed as platinum metal compound solutions, such as a palladium chloride, and again, on the activated carbon particle surface, reduction support of said platinum metal may be carried out, and it may reproduce.

[0009]As for this negative pole carrier, it is preferred to make it not only to accommodate in a cathode room, but flow with processed water, such as selenium ion content waste fluid to supply, and deposit capability by reduction of 6 value selenium declines except for highly acidic Shimo in a fixed-bed type cell to which this flow is not made to perform. Although it is most common to supply said processed water from a lower part of a negative pole carrier, and to perform it as for a means to make this flow cause, other means, such as a mechanical agitation, may perform. a grade of this flow is expressed with an expansion coefficient, and this expansion coefficient shows a value which ^{**}(ed) a value which deducted height (static bed height) of activated carbon etc. which were filled up with a state of rest from height of negative pole carriers (fluid bed), such as activated carbon in the state where it is flowing within a cell, in stillness layer height by percentage. In the usual fluid bed electrolysis, an expansion coefficient exceeds 30%, or it becomes, and is in an intense flow state, and although it is preferred that a maximum of an expansion coefficient also makes this invention about 30%, making it flow exceeding this upper limit does not interfere. Although influence in

selenium reduction efficiency in the state of a flow up to about 20% with a big expansion coefficient is not produced, if it reaches to 30%, in order that reduction efficiency may fall conversely, a desirable expansion coefficient is about 5 to 20%. Since sufficient flow is not obtained with an expansion coefficient being less than 1%, it is desirable to make a lower limit of an expansion coefficient into 1% in this invention. A septum used by this invention is provided in order to prevent a conductive particle in a cathode room from invading in a positive pole room, and if it is an insulating material which has the micropore for energization, there will be no restriction in construction material etc. Therefore, since a cheap material can be used, and there are no worries about blinding and also it is not necessary to supply processed water with high voltage, processed water supply can be performed with a small pump.

[0010]As for other electrolytic conditions, it is desirable to set up as follows.

** The pH of examination waste fluid: 0.8 to 0.5-5.0, especially 1.5.

** current value: 11 - 20 A/kgb-activated carbon (the following "- activated carbon" is omitted) -- especially -- 18 A/kgb order (b of kgb shows beads which means particles).

** Electrolysis solution temperature: Room temperature -45 **.

If it is around one strong acid nature about pH, since oxidation of selenium ion of -2 value occurs, while having good influence on selenium removal efficiency, reduction of 6 value selenium ion will also be promoted. Although reduction efficiency naturally so improves that a current value is high, Although it is desirable to make about 20 A/kgb into a maximum in consideration of an adverse effect to economical efficiency or a device, and a long time is required from a case of 20 A/kgb in the case of a value which exceeds 4 A/kgb a little about a minimum, but selenium ion concentration can be reduced to less than 1mg/l. If it falls to about 3 A/kgb, it will depend on other conditions, but as for said lower limit, since reduction of selenium ion stops almost breaking out, it is preferred to consider it as about 4 A/kgb. It is a grade which can be disregarded and what is necessary is just to perform influence on efficiency under a room temperature or weak heating about electrolysis temperature. Although it is desirable to perform supply of processed water to a cell by a one pass method, it takes out and circulates through processed water once supplied by what is called a batch type out of a cell, and may be made to perform electrolytic treatment.

[0011]If electrolytic treatment of the waste fluid etc. which contain selenium ion, especially 10-20mg/l. of 6 value selenium ion on such conditions is carried out, If selenium ion concentration can be fallen in less than 5mg/l. in about 2 to 6 hours and conditions are further chosen in said conditions, it is made to fall in less than 1mg/l., and selenium ion can be removed substantially. In order to perform in electrolysis

processed water treatment containing this selenium ion, addition drugs are needlessness (since it is pH regulation of processed water, some acid may be added), And processed water which removes all the selenium ion of a variety which has many valences thoroughly depending on conditions from processed water unlike the former, and does not have selenium content is renewable. Although this invention is mainly applied to waste fluid of refinement and selenium ion removal which is an impurity out of said waste fluid, and is an environmental pollutant is made into a key objective more nearly rather than collecting selenium ion as metal selenium, It can apply also to various solutions which contain selenium ion besides this, and may be used for metal selenium recovery.

[0012]Next, an example of electrochemical water treatment equipment concerning this invention is described based on an accompanying drawing. Drawing 1 is drawing of longitudinal section showing an example of batch processing by a cell for processing of selenium content processed water of this invention. 1 is a main part of a cell of a cylindrical shape in which the upper surface carries out an opening.

The processed water feed port 2 is generated in the center of the bottom of this main part 1 of a cell.

The top plate 4 with which the cylindrical anode 3 was inserted in the center is installed in an opening of the upper surface of said main part 1 of a cell, an opening is plugged up, and said anode 3 is wrapped in the saccate acid-proof cloth 5 on which the whole functions as a septum while a lower end arrives at said about two processed water feed port. Inside a flank wall surface of cell 1 main part of said cylindrical shape, the mesh state negative pole 6 of a cylindrical shape is installed, and the activated carbon particle 7 with which catalyst substances, such as palladium, were supported is accommodated in lower space between this negative pole 6 and said acid-proof cloth 5.

[0013]It is connected to the external power 8 and said cylindrical anode 3 and the cylinder negative pole 6 are energized on two poles according to this power supply 8. The treating solution output port 9 is installed in said top plate 4, and in order that this output port 9 may repeat and process liquid processed by said main part 1 of a cell, he is trying to be led to the side and for the other end to reach the treating solution storage tank 10, and to supply it to this tank 10. Circulate through the reservoir water 11 of this tank 10 to said processed water feed port 2 via the filter 13 and the flow instrument 14 with power of the circulating pump 12, and it is introduced from a lower part in the main part 1 of a cell, While maintaining said activated carbon particle 7 in the flow state, processed underwater selenium ion is returned by palladium etc. which were supported by this activated carbon particle 7, and it deposits on the activated carbon

particle 7 surface as metal selenium, or precipitates in the main part 1 of a cell as powder. At this time. Since it is maintained by flow state with processed water which the activated carbon particle 7 which supported a catalyst substance supplies. Since processed underwater selenium ion and contacting efficiency of said catalyst substance improve, it is returned to metal selenium, selenium ion, especially 6 value selenium ion which is hard to be returned deposit comparatively for a short time and it is removed from processed water, Selenium concentration is low or processed processed water whose selenium concentration is zero substantially is taken out from the processed water output port 9.

[0014]

[Example]Next, although the example of the selenium recovery from the processed water containing the selenium ion by this invention is indicated, this example does not limit this invention.

[0015]

[Example 1] Weighing of the palladium chloride 5.2 g was carried out, and sulfuric acid was added to 1 l. of pure water added several drops, and at 60 **, heating stirring was carried out for 1 hour, and it dissolved (3g/(l.) as palladium). Intact activated carbon 0.5 kg was added to this solution, and it was neglected for 2 to 4 hours until liquid became water-white, sometimes stirring. Activated carbon was taken out according to solid liquid separation, and it was made to dry enough at 60 ** (palladium holding amount: 6 g/kgb). In accordance with the wall of the cell of 10 cm in diameter, and 20 cm in height a cylindrical shape, the cylinder negative pole of the mesh state made from titanium was installed, the anode which is the titanium rods which were accommodated in the saccate acid-proof cloth, and which carried out platinum plating was installed in the center, and each was connected to the external power. The processed water feed port was established in the bottom plate of this cell, the processed water stored in the external storage tank was supplied with the pump, after letting a filter pass, and processed water output port was established in the top plate of said cell, and said storage tank was made to circulate through the processed treating solution taken out from this output port.

[0016]It was filled up with said activated carbon particle 0.5 kg which made palladium support in said cell, the expansion coefficient was adjusted with the speed of the processed water supplied to a processed water feed port, and it maintained just over or below 20%. Processed underwater 6 value selenium ion concentration was carried out in 16mg/l., pH was set to 1.0, and it electrolyzed by sending the current of 11 A/kgb, maintaining at 27-34 **, and solution temperature continued electrolysis for 6 hours,

circulating the treating solution taken out from the treating solution output port of the cell to a processed water feed port. When the selenium ion concentration in this treating solution was measured in the treating solution output port of a cell after 18 minutes, 36 minutes, 55 minutes, 73 minutes, 2 hours, and 4-hour progress, they were 14, 13, 12, 10, 6, and <1mg/l., respectively. Although electrolysis was continued for further 2 hours, selenium ion concentration was maintained in less than 1mg/l. This result was summarized in Table 1.

[0017]

[Table 1]

[0018]

[Example 2] The same cell as Example 1 is used and they are [pH] 12 g/kgb and a current value about 23-41 ** and a palladium holding amount in 3.0 and solution temperature 18.0 A/kgb (the pressure value was set to 13.3V) Processed underwater selenium ion was returned on the same conditions as Example 1 except having carried out. Aging of the detection selenium ion concentration in that case was shown in Table 1. Although selenium ion concentration fell to 1mg/l. in 6 hours after an electrolysis start, as compared with Example 1, reduction speed was slow. In spite of having maintained current highly and having increased the palladium holding amount from Example 1, it can be surmised that it is because the pH value was raised to 3 from 1 that whose speed was slow.

[0019]

[Example 3] The place which electrolyzed on the same conditions as Example 2 except having carried out selenium concentration of the thing (temperature also differed a little as Table 1, and the pressure value was set to 8.6 V again) for which the palladium holding amount was not changed and current was made into 11.0 A/kgb as shown in Table 1, and processed water in 1. and 15mg /, The selenium ion concentration after 4-hour progress is 4mg/l. after 8mg [1.] /and 6-hour progress, and reduction speed was falling considerably from Example 2.

[0020]

[Example 4] The place which electrolyzed on the same conditions as substantially as Example 2 except having made palladium holding amount 12 g/kgb of Example 2 into half 6.0 g/kgb as shown in Table 1 (temperature differs from a pressure value slightly as clearly shown in Table 1), the selenium ion concentration in each measuring time is slight as compared with Example 2 -- every -- it is high, the selenium ion concentration after 6-hour progress is 2mg/l. to 1mg/l. of Example 2, and influence on selenium ion reduction of a palladium holding amount was observed.

[0021]

[Example 5] Except having considered it as current (11.0 A/kgb) lower than Example 4 as shown in Table 1, Place which electrolyzed on the same conditions as Example 4 (the pressure value was set to 7.8 V) Although each selenium ion concentration after 4 hours and 6-hour progress was 12 [higher than Example 4] and 4mg/l., sufficient selenium ion reduction was attained.

[0022]

[Reference example 1] The place which electrolyzed on the same conditions as Example 5 except having considered it as current (3.0 A/kgb) still lower than Example 5 as shown in Table 1 (the initial selenium ion concentration of processed water is 18mg/l.).

the pressure value was set to 3.7 V -- the selenium ion concentration after 6-hour progress is 16mg/l., and reduction of substantial selenium ion concentration did not take place.

[0023]

[Reference example 2] what (twice as many 12 g/kgb as this) the palladium holding amount was made for larger than the reference example 1 as shown in Table 1 -- except (the pressure value was set to 4.6 V) . The place which electrolyzed on the same conditions as the reference example 1 (the initial selenium ion concentration of processed water is 16mg/l.), The selenium ion concentration after 6-hour progress is 14mg/l., the reduction from an initial value is the same 2mg/l. as the reference example 1, and it turned out that selenium ion reduction efficiency does not rise even if it will increase a palladium holding amount, if a current value is low.

[0024]

[Comparative example 1] The place which electrolyzed on the same conditions as the reference example 1 except having made the current value into the same 3.0 A/kgb as the reference example 2, and not having performed palladium support to activated carbon (initial selenium ion concentration is 17mg/l.).

the pressure value was set to 6.5 V -- aging of selenium concentration was almost the same as the reference example 2 as it was shown in Table 1.

[0025]

[Comparative example 2] Except having made the current value into the same 11.0 A/kgb as Examples 1, 3, and 5, Place which electrolyzed on the same conditions as the comparative example 1 (the pressure value was set to 12.8V) Aging of selenium concentration was almost the same as the comparative example 1 as it was shown in Table 1, and the selenium ion concentration after 4 hours and 6-hour progress was 14 and 15mg/l. The comparative examples 1 and 2 showed that palladium support was

indispensable in the pH 3.0 above.

[0026]

[Comparative example 3] A palladium holding amount and a current value are made into the same 6 g/kgb as Example 4, and 18 A/kgb, The place which electrolyzed on the same conditions as Example 4 except having controlled the expansion coefficient of activated carbon to less than 1%, and having considered it as the fixed bed substantially (initial selenium ion concentration is 16mg/l., and) the pressure value was set to 15.2V -- it being higher for whether your being Haruka than Example 4 as aging of selenium concentration is shown in Table 1, and, The selenium ion concentration after 4 hours and 6-hour progress was 17 and 14mg/l., and when the expansion coefficient of activated carbon was made into less than (substantial fixed bed) 1%, it turned out that reduction of selenium ion hardly takes place.

[0027]

[Comparative example 4] The place which electrolyzed on the same conditions as the making [did not make activated carbon support palladium and / fluctuate a little]-current value (16 A/kgb) comparative example 3 (initial selenium ion concentration is 17mg/l.), There is no big change at a grade slightly smaller than the comparative example 3 as aging of selenium concentration is shown in Table 1, and it turned out that the existence of the palladium support by an expansion coefficient being less than (substantial fixed bed) 1% hardly affects efficiency.

[0028]

[Examples 6-8] Hold uniformly pH, a palladium holding amount, and an expansion coefficient, and a current value Example 6 (5.0 A/kgb), When Example 7 (11.0 A/kgb) and Example 8 (18.0 A/kgb), and order were raised, the same electrolysis as Examples 1-5 was performed and aging was measured, the result was as being shown in Table 2. The time taken for selenium ion concentration to reach in less than 1mg/l. was 10 hours (example 6), 6 hours (example 7), and 2 hours (example 8), respectively, and it turned out that selenium ion reduction takes place for a short time, so that the current value was high.

[0029]

[Table 2]

[0030]

[Examples 9-11] pH, a palladium holding amount, and a current value are held uniformly, and it is Example 9 (10%) about the expansion coefficient of activated carbon. When the rate of flow of processed water raised a part for 2 and 5L/, Example 10 (the 20% rate of flow is a part for 3 and 6L/) and Example 11 (% [30] and the rate of flow are

parts for 5 and 0L/), and order, and performed the same electrolysis as said example and aging was measured, the result was as being shown in Table 2. The time taken for selenium ion concentration to reach in less than 1mg/l. is 2 hours (example 9), 2 hours (example 10), and 6 hours (example 11), respectively, and said expansion coefficient was understood that 10 to 20% is suitable.

[0031]

[Examples 12-13] When the same electrolysis as Example 8 was substantially performed on the same conditions with Example 8 (pH 1.0) except having set pH to 0.8 and (example 12) 1.5 (example 13) and aging was measured, the result was as being shown in Table 2. Although both are 3 hours and had required time rather than 2 hours of Example 3, as for the time taken for selenium ion concentration to reach [1.] in less than 1mg /, it turned out that pH reaches early whether you are Haruka in less than 1mg/l. rather than Examples 2-5 which are 3.

[0032]

[Examples 14-18] Fixed in pH, a palladium holding amount, a current value, and an expansion coefficient (pH 1.0, current value 18.0 A/kgb, 10% of expansion coefficient) In order to hold and to check experimental reproducibility, when the same electrolysis as said each example was performed and aging was measured, the result was as being shown in Table 2. The time taken for selenium ion concentration to reach in less than 1mg/l., respectively 4 hours (example 14), It is 3 hours (example 15), 3 hours (example 16), 3 hours (example 17), and 4 hours (example 18), and it turned out that even a desired level is decreased in the selenium ion concentration in a treating solution by electrolysis of 3 to 4 hours.

[0033]

[Example 19] pH 1.0, current value 9.0 A/kgb, palladium holding amount 6 g/kgb, When it was considered as 10% of the expansion coefficient, initial selenium ion concentration electrolyzed the processed water which is 10mg/l. and consumption quantity of electricity and the relation of residual selenium ion were measured, the result was as being shown in drawing 2. (the pressure value was set to 6.5 V) . In consumption quantity of electricity, selenium ion concentration became zero mostly in 1.8 Ahr/a liter. The pressure value at this time was 6.4 V.

[0034]

[Comparative example 5] Place which electrolyzed on the same conditions as Example 19 except having set the palladium holding amount to 0g / kgb, and measured consumption quantity of electricity and the relation of residual selenium ion (the pressure value was set to 7.6 V) The result was as being shown in drawing 2. Even if

consumption quantity of electricity became 5.4 Ahr/a liter, selenium ion concentration was about 1mg/l., and it turned out without palladium support that sufficient selenium ion removal does not take place. The pressure value at this time was 6.7 V.

[0035]

[Effect of the Invention]This invention to this cathode room of the fluid bed type cell which accommodated the conductive particle which supported 1 or two or more platinum metals in this cathode room of the cell divided by the septum in the positive pole room and the cathode room. It is a disposal method (claim 1) of the selenium content processed water supplying and electrolyzing the processed water containing 6 value selenium, returning said 6 value selenium, and considering it as metal selenium or an insoluble selenium compound. The technique of even metal returning and depositing and removing 6 value selenium which is hard to be returned from a solution in the deposit by reduction of the conventional selenium ion, is that the most carries out using a strong reducing agent, By this technique, there was a problem that condition regulation was difficult, a reducing agent remained in a solution again, and that separation also took time and effort. In spite of having requested that removal of 6 value selenium ion should carry out on comparatively quiet conditions, it did not hit on an idea of the feasible 6 value selenium removal method industrially.

[0036]Although there is electrolysis as a means by which a reduction reaction can be carried out by a comparatively quiet reducing condition, 6 value selenium cannot be returned in mere electrolysis. this invention person is what reached this invention, as a result of examining various the techniques of returning in electrolysis 6 value selenium which is hard to be returned in this way, It is the fluid bed type cell which accommodated the negative pole carrier which comprises the conductive particle which supported the platinum metal etc., and makes it possible to return 6 value selenium and to consider it as metal selenium or an insoluble selenium compound by processing the processed water containing 6 value selenium. In this invention in which 6 value selenium removal of 0.5-3.0 (claim 3) is meant, large pH range, i.e., pH, support of a platinum metal and flow of a negative pole carrier are indispensable requirements, and even if any are missing, 6 value selenium is no longer deposited in electrolysis. However, in the pH 1.0 neighborhood, even if there is no support of a platinum metal, removal of 6 value selenium is possible. As said platinum metal, palladium is the optimal (claim 2).

[0037]It means that that 6 value selenium can be returned returns and tetravalence and divalent selenium are also deposited in it, and in order that the selenium of -2 value may oxidize easily that especially a solution is acidity to divalent or tetravalence, all the selenium ion of -2, 2 and 4, and 6 values can be returned by this invention. this

invention method can also be enforced using the fixed-bed type cell which accommodated not only the fluid bed type cell that accommodated the conductive particle mentioned above but the conductive fiber (claim 4). Without being efficient on comparatively quiet conditions similarly, and producing a residual impurity also by this method, 6 value selenium can be returned and removal from processed water is attained.

[Brief Description of the Drawings]

[Drawing 1] Drawing of longitudinal section showing an example of the cell for processing of the selenium content processed water of this invention.

[Drawing 2] The graph which shows consumption quantity of electricity in Example 19 and the comparative example 6, and the relation of residual selenium ion.

[Description of Notations]

1 ... Main part of a cell 2 ... Waste fluid feed port 3 ... Cylindrical anode 4 ... Top plate
5 ... Acid-proof cloth 6 ... Negative pole 7 ... Activated carbon 8 ... Power supply 9 ...
Waste fluid output port 10 ... Waste fluid storage tank 11 ... Reservoir water 12 ... Waste
fluid feed port 13 ... Filter 14 ... Flow instrument

DRAWINGS

[Drawing 1]

[Drawing 2]
